

What is claimed is:

1. A method for preparing the surface of dentin or enamel for adhesion of composite materials or resins, which method comprises:

(a) contacting with the surface of the dentin or enamel an aqueous solution or solutions comprising (1) at least on acidic salt containing a polyvalent cation which is capable of changing valence by unit steps and which can bind to dentin or enamel surface sites, and at least one anion which forms a relatively water-insoluble precipitate or precipitates with calcium and which contains at least one carboxyl group; and (2) acid;

(b) contacting with the surface of the dentin or enamel a solution comprising at least one compound selected from the group consisting of (1) N-phenylglycine, (2) the adduct of N(p-tolyl)glycine and glycidyl methacrylate, and (3) the addition reaction product of N-phenylglycine and glycidyl methacrylate in a solvent; and

(c) contacting with the surface of the dentin or enamel a solution comprising at least one compound selected from the group consisting of (1) the addition reaction product of pyromellitic acid dianhydride and 2-hydroxyethyl methacrylate, (2) the addition reaction product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2-hydroxyethyl methacrylate, and (3) 4-methacryloxyethyltrimellitic anhydride.

2. A method as in claim 1 wherein the concentration of the acidic salt solution is from about 0.1% to a saturated solution.

3. A method as in claim 1 wherein the cation of the acidic salt forms a relatively insoluble phosphate.

4. A method as in claim 1 wherein the acidic salt is ferric oxalate.

5. A method as in claim 1 wherein the acidic salt is ferric citrate.

6. A method as in claim 1 wherein the acid is nitric acid.

7. A method as in claim 1 wherein the concentration of the solution comprising at least one compound selected from the group consisting of (1) N-phenylglycine, (2) the adduct of N(p-tolyl)glycine and glycidyl methacrylate, and (3) the addition reaction product of N-phenylglycine and glycidyl methacrylate in a solvent is from about 0.1% to a saturated solution.

8. A method as in claim 1 wherein the concentration of the solution of at least one compound selected from the group consisting of (1) the addition reaction product of pyromellitic acid dianhydride and 2-hydroxyethyl methacrylate, (2) the addition reaction product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2-hydroxyethyl methacrylate, and (3) 4-methacryloxyethyltrimellitic anhydride is from about 0.1% to a saturated solution.

9. A method as in claim 1 wherein the solvent for the solution of subpart (b) is acetone.

10. A method as in claim 1 wherein the solvent for the solution of subpart (c) is acetone.

11. A method as in claim 1 wherein the steps (a), (b) and (c) are performed in that order.

12. A method for preparing the surface of dentin or enamel for adhesion of composite materials or resins, which method comprises:

(a) contacting the surface of the dentin or enamel with an aqueous solution comprising ferric oxalate and nitric acid;

(b) washing and then drying the surface of the dentin or enamel;

(c) contacting the surface of the dentin or enamel with a first acetone solution comprising at least one compound selected from the group consisting of (1) N-phenylglycine, (2) the adduct of N(p-tolyl)glycine and glycidyl methacrylate, and (3) the addition reaction product of N-phenylglycine and glycidyl methacrylate in acetone;

(d) removing any excess of the first acetone solution and rinsing the surface of the dentin or enamel with acetone, removing any excess acetone and drying the surface;

(e) contacting the surface of the dentin or enamel with a second acetone solution comprising at least one compound selected from the group consisting of (1) the addition reaction product of pyromellitic acid dianhydride and 2-hydroxyethyl methacrylate and (2) the addition reaction product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2-hydroxyethyl methacrylate.

13. A method as in claim 12 wherein the concentration of ferric oxalate in the aqueous solution comprising ferric oxalate and nitric acid is about 6.8% of the hexahydrate.

14. A method as in claim 12 wherein the concentration of nitric acid in the aqueous solution comprising ferric oxalate and nitric acid is between 0 and 50%.

15. A method as in claim 12 wherein the concentration of nitric acid in the aqueous solution comprising ferric oxalate and nitric acid is between about 0.068 and about 10%.

16. A method as in claim 12 wherein the concentration of nitric acid in the aqueous solution comprising ferric oxalate and nitric acid is about 0.68%.

17. A method as in claim 12 wherein the concentration of nitric acid in the aqueous solution comprising ferric oxalate and nitric acid is about 2.5%.

18. A method as in claim 12 wherein the concentration of ferric oxalate in the aqueous solution comprising ferric oxalate and nitric acid is about 4% of the hexahydrate.

19. A method as in claim 12 wherein the washing medium is water.

20. A method as in claim 12 wherein the compound in the first acetone solution is N-phenylglycine.

21. A method as in claim 12 wherein the concentration of the compound in the first acetone solution is about 10% of the N-phenylglycine in acetone.

22. A method as in claim 12 wherein the compound in the second acetone solution is the addition reaction product of pyromellitic acid dianhydride and 2-hydroxyethyl methacrylate.

23. A method as in claim 22 wherein the concentration of the compound in the second acetone solution is about 5%.

24. A method for preparing the surface of dentin, enamel or industrial substrates for adhesion of composite materials or resins, which method comprises:

(a) contacting with the surface of the dentin, enamel or industrial substrate an aqueous solution or solutions comprising (1) at least one acidic salt containing a polyvalent cation which is capable of changing valence by unit steps and which can bind to dentin, enamel, or industrial substrate surface sites, and at least one anion which forms a relatively water-insoluble precipitate or precipitates with